

## CLAIMS

1. A method of manufacturing an article of manufacture for use in a fluxless brazing process, the method comprising the steps of providing a substrate comprising aluminum; applying to the substrate a bonding layer which comprises one or more metals selected from the group consisting of zinc, tin, lead, bismuth, nickel, antimony and thallium, and applying to the bonding layer a braze-promoting layer including one or more metals selected from the group consisting of nickel, cobalt and iron, the bonding layer and the substrate defining a target surface of the substrate at the junction therebetween.
2. A method according to claim 1, wherein the braze-promoting layer comprises nickel and is plated onto the bonding layer.
3. A method according to claim 2, wherein the bonding layer comprises zinc or tin.
4. A method according to claim 3, wherein the article of manufacture is a brazing sheet product, the substrate comprises brazing sheet including a core layer and a clad layer formed of a brazing alloy including aluminum and 2-18% silicon, the clad layer having the target surface defined thereon, and further including the preliminary step of applying the bonding layer to the target surface.
5. A method according to claim 3, wherein the article of manufacture is a brazing sheet product, the substrate comprises brazing sheet including a core layer and a clad layer formed of a brazing alloy including aluminum, the clad layer having the target surface defined thereon, and further including the preliminary step of applying the bonding layer to the target surface.

6. A method according to claim 3, wherein the article of manufacture is a brazeable object, the substrate comprises an object to be rendered brazeable formed from brazing sheet including a core layer and a clad layer formed of a brazing alloy including aluminum and having the target surface defined thereon, and further including the preliminary step of applying the bonding layer to the target surface.
7. A method according to claim 3, wherein the article of manufacture is a brazing preform, the substrate comprises a brazing alloy including aluminum and having the target surface defined thereon, and further including the preliminary step of applying the bonding layer to the target surface.
8. A method according to claim 1, further comprising the preliminary step of applying the bonding layer to the target surface.
9. A method according to claim 8, wherein the application of the bonding layer is preceded by mechanical abrasion of the substrate such that the target surface defines a plurality of reentrant edges.
10. A method according to claim 9, wherein the mechanical abrasion constitutes a brush cleaning of the surface.
11. A method according to claim 10, wherein the brush cleaning is affected through nylon or stainless steel brushes.
12. A method according to claim 11, wherein the bonding layer is applied by an immersion zincate treatment.

13. A method of manufacturing an article of manufacture for use in an improved fluxless brazing process, the method comprising the steps of providing a substrate containing aluminum; plating a braze-promoting layer selected from the group consisting of nickel and cobalt onto the substrate, the junction of the braze-promoting layer and the substrate defining a target surface of the substrate; and prior to the step of plating the braze-promoting layer onto the substrate, mechanically abrading the substrate such that the target surface defines a plurality of reentrant edges.
14. A method according to claim 13, wherein the mechanical abrasion constitutes a brush cleaning of the surface.
15. A method according to claim 14, wherein the brush cleaning is delivered by nylon or stainless steel brushes.
16. A method of manufacturing an article of manufacture for use in a fluxless brazing process, the method comprising the step of providing a substrate containing aluminum; electroplating a braze-promoting layer including one or more metals selected from the group consisting of nickel and cobalt onto the substrate, wherein the electroplating is carried out in an aqueous bath having a pH of from about 5 to 7 and including, in solution, said one or more metals.
17. A method according to claim 16, wherein the bath further comprises citrate in solution.
18. A method according claim 17, wherein the bath further comprises ammonium in solution.
19. A method according to claim 18, wherein the mole ratio of nickel: citrate: ammonium in solution is about 1: 0.5 - 1.5: 1-6.

20. A method of manufacturing an article of manufacture for use in a fluxless brazing process, the method comprising the steps of providing a substrate containing aluminum; and electroplating a braze-promoting layer containing nickel onto the substrate, wherein the electroplating is carried out in an aqueous bath consisting of an aqueous solution of:

from about 3 to about 20 weight percent of nickel sulfate;

from about 3 to about 10 weight percent of nickel chloride;

from about 6 to about 30 weight percent of a buffering salt selected from the group consisting of sodium citrate and sodium gluconate;

from about 0.005 to about 1.0 weight percent of a lead salt selected from the group consisting of lead acetate and lead citrate; and

ammonium,

wherein the bath has a pH value in the range of about 3 to 12 and has a mole ratio of nickel: citrate: ammonium in solution of about 1: 0.5 - 1.5: 1-6.

21. A method of manufacturing an article of manufacture for use in a fluxless brazing process, the method comprising the steps of providing a substrate containing aluminum; plating a braze-promoting layer containing nickel onto the substrate, wherein the electroplating is carried out in an aqueous bath consisting of an aqueous solution of nickel, citrate and ammonium, and wherein the plating bath has a pH value in the range of about 5 to 12 and has a mole ratio of nickel: citrate: ammonium in solution of about 1: 0.5 - 1.5: 1-6.

22. A method according to claim 21, wherein the braze-promoting layer is applied by electroplating in which one or more process parameters are selected from:
- (a) electroplating bath temperature 20-70°C;
  - (b) electroplating bath pH 4.0-12.0;
  - (c) current density of 0.1-15.0 A/dm<sup>2</sup>;
  - (d) plating time 1 to 300 s, preferably 30 to 120s; and
  - (e) bath composition including 0-300 g/l nickel sulfate, 0-225 g/l nickel chloride, 50-300 g/l sodium citrate, 0.05-10.0 g/l lead acetate, and 5-325 ml/l ammonium hydroxide (calculated as 30% ammonium hydroxide solution).
23. A method according to claim 21, wherein the braze-promoting layer is applied by electroplating having process parameters as follows:
- (a) electroplating bath pH about 8.1; and
  - (b) bath composition including about 70 g/l nickel sulfate, 30 g/l nickel chloride, 120 g/l sodium citrate, 20 g/l sodium acetate, 15 g/l ammonium sulfate, 1 g/l lead acetate, and 30 ml/l ammonium hydroxide (calculated as 30% ammonium hydroxide solution).

24. A method according to claim 21, wherein the braze-promoting layer is applied by electroplating having process parameters as follows:
- (a) electroplating bath pH about 7.8; and
  - (b) bath composition including about 70 g/l nickel sulfate, 30 g/l nickel chloride, 120 g/l sodium citrate, 20 g/l sodium acetate, 50 g/l ammonium chloride, 1 g/l lead acetate, and 30 ml/l ammonium hydroxide (calculated as 30% ammonium hydroxide solution).
25. A method according to claim 21, wherein the braze-promoting layer is applied by electroplating having process parameters as follows:
- (a) electroplating bath pH about 7.8; and
  - (b) bath composition including about 155 g/l nickel chloride, 110 g/l sodium citrate, 100 g/l ammonium chloride, 1 g/l lead acetate, and 146 ml/l ammonium hydroxide (calculated as 30% ammonium hydroxide solution).
26. A method according to claim 25, wherein the bath further comprises about 66 g/l sodium gluconate.
27. A method according to claim 21, wherein the braze-promoting layer is applied by electroplating having process parameters as follows:
- (a) electroplating bath pH about 7.6; and
  - (b) bath composition including about 150 g/l nickel chloride, 200 g/l sodium citrate, 20 g/l ammonium chloride, 1 g/l lead acetate, and 30 ml/l sodium hydroxide (calculated as 25% sodium hydroxide solution).

28. A method according to claim 16, wherein the braze-promoting layer is applied by electroplating having process parameters as follows:
- (a) electroplating bath pH about 6.4; and
  - (b) bath composition including about 155 g/l nickel chloride, 1 g/l lead acetate, 154 g/l EDTA and 93 ml/l ammonium hydroxide (calculated as 30% ammonium hydroxide solution).
29. A method according to claim 2, wherein the braze-promoting layer is applied by electroplating in an aqueous bath including nickel, in solution, and an acid sufficient to adjust the pH of such bath to between about 3-7.
30. A method according to claim 29, wherein the bath further comprises ammonium in solution.
31. A method according to claim 30, wherein the bath further comprises lead.
32. A method according to claim 31, wherein the electroplating is carried out with process parameters as follows:
- (a) electroplating bath temperature 25-30°C;
  - (b) electroplating bath pH in the range of 4.8 to 5.2;
  - (c) current density of 50 mA/cm<sup>2</sup>;
  - (d) plating time 1 to 300 seconds; and
  - (e) bath composition including about 150 g/l nickel sulphate, 30 g/l ammonium chloride, 1 g/l lead acetate and 30 g/l boric acid.

33. A method according to claim 31, wherein the electroplating is carried out with process parameters as follows:
- (a) electroplating bath temperature 25-30°C;
  - (b) electroplating bath pH in the range of 3.2 to 6.2, controlled with sulphuric, acetic or hydrochloric acid;
  - (c) current density of 50 mA/cm<sup>2</sup>;
  - (d) plating time 1 to 300 seconds; and
  - (e) bath composition including about 100 g/l nickel chloride, 5-150 g/l sodium citrate, 1 g/l lead acetate and 5 - 100 g/l ammonium chloride.
34. A method according to claim 33, wherein the bath composition further comprises 30 g/l boric acid.
35. An article of manufacture for use in an improved fluxless brazing process, comprising a substrate containing aluminum; a bonding layer on the substrate selected from the group of metals consisting of zinc, tin, lead, bismuth, nickel, antimony and thallium; and a braze-promoting layer on the bonding layer, the braze-promoting layer being selected from the group consisting of nickel, cobalt and iron.
36. An article according to claim 35, wherein the braze-promoting layer comprises nickel and the bonding layer comprises zinc or tin.
37. An article according to claim 36, wherein the bonding layer comprises zinc.



38. An article according to claim 36, wherein the article of manufacture is a brazing sheet product, wherein the substrate comprises brazing sheet including a core layer and a clad layer formed of a brazing alloy including aluminum and 2-18% silicon, and the bonding layer is disposed on the clad layer.
39. An article according to claim 36, wherein the article of manufacture is a brazing sheet product, wherein the substrate comprises brazing sheet including a core layer and a clad layer formed of a brazing alloy including aluminum, and the bonding layer is disposed on the clad layer.
40. A brazing sheet product according to claim 38, wherein the braze-promoting layer comprises lead or bismuth.
41. A brazing sheet product according to claim 40, wherein the braze-promoting layer comprises lead.
42. A brazing sheet product according to claim 39, wherein the braze-promoting layer has a thickness of not more than about 2.0  $\mu\text{m}$ , preferably, between 0.5-1.0  $\mu\text{m}$ .
43. A brazing sheet product according to claim 42, wherein the bonding layer has a thickness of not more than 0.5  $\mu\text{m}$ , preferably not more than 0.3 $\mu\text{m}$ .
44. A brazing sheet according to claim 43, wherein the bonding layer comprises lead and the braze-promoting layer comprises nickel.
45. A brazing sheet according to claim 43, wherein the bonding layer comprises nickel and lead and the braze-promoting layer comprises nickel.

46. A brazing sheet according to claim 43, wherein the bonding layer comprises zinc or tin, and the braze-promoting layer is a duplex layer including an inner layer including nickel and lead or nickel and bismuth and an outer layer including nickel.
47. An article according to claim 39, wherein, taken together, said clad layer and all layers exterior thereto, have a composition containing at least one of the following elements:
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|----|--|
| Th | in the range 0.01 to 1.0% by weight;     |
| Bi | in the range 0.01 to 0.5% by weight;     |
| Mg | in the range 0.05 to 2.0% by weight;     |
| Li | in the range 0.01 to 0.5% by weight; and |
| Pb | in the range 0.01 to 1.0% by weight.     |
48. An article according to claim 39, wherein said bonding layer contains by weight an amount not more than 50% in total of one or more elements selected from bismuth, lead, lithium and antimony.
49. An article according to claim 39, wherein said clad layer contains by weight Zn in an amount in the range of up to about 5%.
50. An article according to claim 36, wherein the article of manufacture is a brazing preform and wherein the substrate comprises a brazing alloy.
51. An article according to claim 50, wherein the brazing alloy comprises 2-18% silicon.

52. Use of a brazing preform according to claim 50 to braze :
- (a) aluminum to aluminum or to any aluminized metal;
  - (b) nickel-coated titanium or steel to aluminum or to any aluminized metal; or
  - (c) nickel-coated titanium or steel to nickel-coated titanium or steel.
53. An assembly of components joined by brazing, at least one said components being formed from one of a brazing sheet product according to claim 39 and a brazeable object formed according to claim 6.
54. A method of manufacturing an assembly of brazed components, comprising the steps of:
- (a) providing said components, at least one of which is made from one of a brazing sheet product according to claim 39 and a brazeable object made according to claim 6;
  - (b) forming said components into an assembly;
  - (c) brazing the assembly in a non-oxidizing environment in the absence of a brazing flux at elevated temperature for a period long enough for melting and spreading of the clad layer; and
  - (c) cooling the brazed assembly.
55. A method according to claim 54, wherein the non-oxidizing environment is a vacuum or an inert atmosphere.
56. A method according to claim 1, wherein the bonding layer comprises nickel and lead, bismuth or thallium.